<Division of Environmental Chemistry> Hydrospheric Environment Analytical Chemistry

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- Hydrospheric Environment Analytical Chemistry -

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Assoc Scientist SAITO, Mak Anderson Woods Hole Oceanographic Institution, USA, 3 July 2007

Scope of Research

Research activities are concerned with geochemistry, oceanography, limnology and analytical chemistry, which are important basic sciences in order to realize the sustainable society. Major research subjects are as follows: (i) Biogeochemistry of trace elements in the hydrosphere. The study also covers hydrothermal activity and deep biosphere. Major parts of these studies are based on field works. (ii) Iron uptake mechanism of phytoplankton. (iii) Ion recognition.

Research Activities (Year 2007)

Publications

Firdaus M L, Norisuye K, Sato T, Urushihara S, Nakagawa Y, Umetani S, Sohrin Y: Preconcentration of Zr, Hf, Nb, Ta and W in Seawater Using Solid-phase Extraction on TSK-8-hydroxyquinoline Resin and Determination by Inductively Coupled Prasma-mas Spectrometry, *Anal. Chim. Acta*, **583**, 296-302 (2007).

Norisuye K, Ezoe M, Nakatsuka S, Umetani S, Sohrin Y: Distribution of Bioactive Trace Metals (Fe, Co, Ni, Cu, Zn and Cd) in the Sulu Sea and Its Adjacent Seas, *Deep-Sea Res. II*, **54**, 14-37 (2007).

Nakatsuka S, Okamura K, Norisuye K, Sohrin Y: Simultaneous Determination of Suspended Particulate Trace Metals (Co, Ni, Cu, Zn, Cd and Pb) in Seawater with Small Volume Filtration Assisted by Microwave Digestion and Flow Injection Inductively Coupled Plasma Mass Spectrometer, *Anal. Chim. Acta*, **594**, 52-60 (2007).

Presentations

Simultaneous Determination of Key Trace Metals in Seawater, Sohrin Y, GEOTRACES Pacific Basin Workshop, 27 June 2007.

Development of Chelate Resin Column Preconcentration Method for Precise Isotope Analysis of Mo in Seawater, Nakagawa Y, Mochamad L F, Norisuye K, Sohrin Y, Irisawa K, Hirata T, 17th Annual V.M. Goldschmidt Conference 2007, 21 August 2007.

Physicochemical Speciation of Trace Metals during the Mesoscale Iron Enrichment (SEEDS II) in the Western North Pacific, Nakatsuka S, Sohrin Y, Norisuye K, Okamura K, Takeda S, Nishioka J, 17th Annual V.M. Goldschmidt Conference 2007, 23 August 2007.

Molecular Design of Extraction Reagents of High Selectivity Based on Steric Factors, Umetani S, Fukui Y, Sohrin Y, Uezu K, The 56th Annual Meeting of the Japan Society for Analytical Chemistry, 20 September 2007.

Simultaneous Determination of Trace Metals in Seawater Using NOBIAS CHLATE-PA1 and Its Application to the Bering Sea and the Arctic Ocean, Minami T, Urushihara S, Nakatsuka S, Higo E, Norisuye K, Sohrin Y, International Symposium on Metallomics 2007, 29 November 2007.

Development of Solid-phase Extraction Method Using Chelating Resin for Precise Isotope Analysis of Mo in Seawater

The behaviors of Mo in oxic environments are different from those in anoxic environments. The degree of isotopic fractionations in reactions of Mo in each environment is also different. Figure 1 shows reported Mo isotope ratios in natural samples. Using the isotopic information, the global material balance and circulation of Mo and the redox status of paleocean can be clearly estimated.

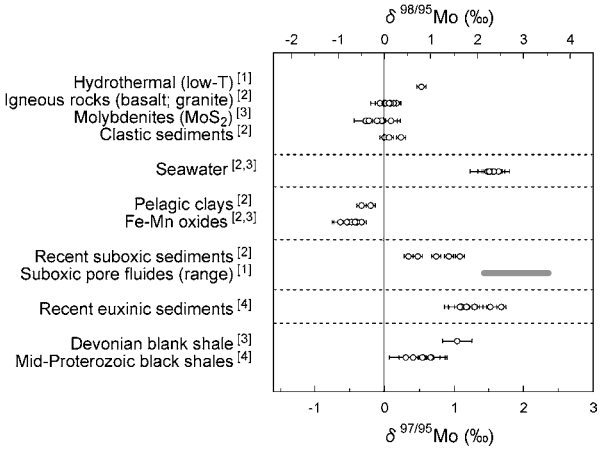

Figure 1. Summary of existing Mo isotope data from natural samples.

For geochemical studies, the isotope ratios in seawater are important reference values, and therefore precise and accurate analytical methods are required. In reported analytical methods, anion exchange resins have been used for separation and enrichment of Mo. These methods possess high procedure blank and low analytical precision and reliability, because the methods require complicated procedures with concentrated acid for elution. The methods give incomplete separation of major elements in seawater. Because of these reasons, although the reported isotopic ratios of Mo in seawater are scarce, they show a large variation. We have developed a solid-phase extraction method using chelating resin to resolve such problems.

TSK-8HQ [5] was used in a column to concentrate Mo. The sample solution that had been adjusted to pH 2.0 with HCl was passed through the column, and then the adsorbed Mo was eluted by the back flushing of 2 M NH_3. The eluate was then evaporated to dryness using a closed evaporation system, and then Mo was re-dissolved in 5 mL of 0.05% tetramethylammonium hydroxide solution. Mo isotope ratios were determined by multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS).

Seawater samples were collected from 3 stations in the western North Pacific Ocean during the MR05-01 cruise of R/V Mirai using a CTD carousel on which Niskin-X samplers were mounted. Seawater was filtered through a 0.2 μm Nuclepore filter and acidified to pH 2.2 with HCl.

Mo was quantitatively concentrated from 250 mL seawater with a 50-fold concentration factor through the column extraction and evaporation. Procedure blank was only 0.04% of the concentration of Mo in seawater. The residual ratios of major elements between the eluate and seawater were below 10^{-5}, and their matrix effects on Mo isotope analysis were negligible. The isobaric interference of ions of coexistent elements was also negligible.

The analytical precision of this method was higher than that of reported methods. Isotope ratios of Mo show uniform vertical profiles at all 3 stations. This is attributed to homogenization of Mo in the ocean, because Mo has a longer mean residence time (~10^5-10^6 years [6]) than ocean circulation time (~10^3 years). The overall variation of isotope ratios of Mo in seawater was smaller than previously reported.

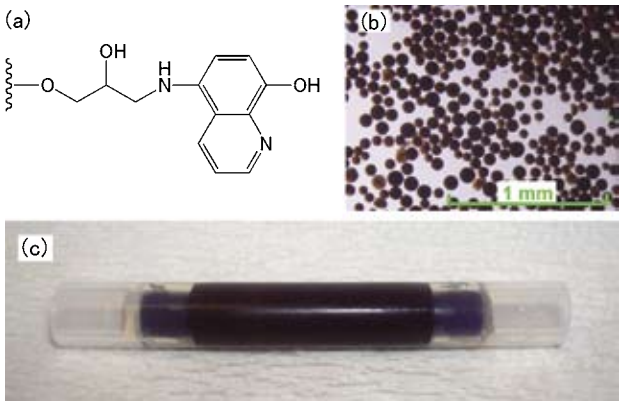

Figure 2. (a) Structure of TSK-8HQ (b) A micrograph of TSK-8HQ (c) A picture of TSK-8HQ column.

This is a joint research with associate professor Takafumi Hirata, Tokyo Institute of Technology.

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[2] C. Siebert *et al.*, *Earth Planet. Sci. Lett.* **211**, 159 (2003).
[3] J. Barling *et al.*, *Earth Planet. Sci. Lett.* **193**, 447 (2001).
[4] G. L. Arnold *et al.*, *Science* **304**, 87 (2004).
[5] H. Dierssen *et al.*, *Mar. Chem.* **73**, 173 (2001).
[6] J. L. Morford *et al.*, *Geochim. Cosmochim. Acta* **63**, 1735 (1999).

Grants

Sohrin Y, Interaction between Metallome and Proteome in the Marine Ecosystem, Grant-in-Aid for Scientific Research (A) (2), 1 April 2004–31 March 2007.

Norisuye K, Development of Analytical Method for Unstable Fe(II) in Seawater Based on in situ Preconcentration, Grant-in-Aid Young Scientists B, 1 April 2006–31 March 2008.